

Table 1: Global annual emission fluxes in the model (Tg S yr⁻¹)

Source	SO ₂	H ₂ S	DMS	Total
Biosphere		0.41	0.29	0.70
Biomass Burning	2.99			2.99
Ocean			20.7	20.7
Man-made	64.59	2.82		67.41
Total	67.58	3.23	20.99	91.8

5 % of man-made SO₂ is emitted directly as sulfate.

Table 2: Rate Reactions for Gas-Phase Chemistry

R.No.	Reaction	Rate
1.	O ₃ + hν → O(¹ D) + O ₂	$j_1 = 1.5 \times 10^{-5}$
2.	O(¹ D) + O ₂ (+M) → O ₃ (+M)	$k_2 = 3.2 \times 10^{-11} \exp(67/T)$
3.	O(¹ D) + H ₂ O → 2 OH	$k_3 = 2.2 \times 10^{-10}$
4.	CH ₄ + OH + O ₂ → CH ₃ O ₂ + H ₂ O	$k_4 = 3.9 \times 10^{-12} \exp(-1885/T)$
5.	CH ₃ O ₂ + NO → CH ₃ O + NO ₂	$k_5 = 4.2 \times 10^{-12} \exp(180/T)$
6.	CH ₃ O + O ₂ → CH ₂ O + HO ₂	$k_6 = 7.2 \times 10^{-14} \exp(-1080/T)$
7a.	CH ₂ O + hν → CO + H ₂	$j_{7a} = 70\% \text{ of } k_6$
7b.	CH ₂ O + hν + 2O ₂ → CO + 2HO ₂	$j_{7b} = 30\% \text{ of } k_6$
8.	CO + HO(+O ₂) → CO ₂ + HO ₂	$k_8 = 1.5 \times 10^{-13}(1+0.6P)$
9.	HO ₂ + NO → HO + NO ₂	$k_9 = 3.7 \times 10^{-12} \exp(240/T)$
10.	HO ₂ + O ₃ → OH + 2O ₂	$k_{10} = 1.4 \times 10^{-14} \exp(-600/T)$
11.	HO ₂ + HO ₂ → H ₂ O ₂ + O ₂	$k_{11} = 2.2 \times 10^{-13} \exp(600/T) + 1.9e-33 \exp(980/T) M$
12.	H ₂ O ₂ + hν → 2HO	$j_{12} = 5 \times 10^{-6}$
13.	H ₂ O ₂ + OH → HO ₂ + H ₂ O	$k_{13} = 2.9 \times 10^{-12} \exp(-160/T)$
14.	SO ₂ + OH → H ₂ SO ₄ + HO ₂	$k_{14} = 2 \times 10^{-12}$
15.	NO ₂ + OH (+M) → HNO ₃ + M	$k_{15} = 6 \times 10^{-11}$
16.	NO + O ₃ → NO ₂ + O ₂	$k_{16} = 1.8 \times 10^{-12} \exp(-1370/T)$
17.	NO ₂ + hν → NO + O	$j_{17} = 7 \times 10^{-3}$
18.	NO ₂ + O ₃ → NO ₃ + O ₂	$k_{18} = 1.2 \times 10^{-13} \exp(-2450/T)$
19.	HNO ₃ + OH → NO ₃ + H ₂ O	$k_{19} = a$
20.	NO ₃ + NO → NO ₂ + NO ₂	$k_{20} = 1.5 \times 10^{-11} \exp(170/T)$
21.	NO ₃ + NO ₂ + M → N ₂ O ₅ + M	$k_{21} = b$
22.	N ₂ O ₅ + M → NO ₂ + NO ₃	$k_{22} = c$
23.	N ₂ O ₅ + hν → NO ₂ + NO ₃	$j_{23} = 5.04 \times 10^{-5}$
24.	NO ₃ + hν → NO ₂ + O ₃	$j_{24} = 2.84 \times 10^{-1}$
25.	NO ₃ + hν → NO + O ₂	$j_{25} = 2.5 \times 10^{-2}$
26.	HNO ₃ + hν → NO ₂ + OH	$j_{26} = 8.26 \times 10^{-6}$
27.	OH + O ₃ → HO ₂ + O ₂	$k_{27} = 1.6 \times 10^{-12} \exp(-940/T)$
28.	HO ₂ + OH → H ₂ O + O ₂	$k_{28} = 4.8 \times 10^{-11} \exp(250/T)$
29.	DMS + OH → SO ₂ + 2HCHO + MSA	$k_{29} = 9.6 \times 10^{-12} \exp(-234/T)$
30.	H ₂ S + OH → SO ₂ + HO ₂	$k_{30} = 6 \times 10^{-12} \exp(-75/T)$
31.	DMSO + OH → 0.6SO ₂ + 0.4MSA + 1.5HCHO	$k_{31} = 5.8 \times 10^{-11}$
32.	DMS + OH → 0.6SO ₂ + 0.4DMSO + 1.2HCHO	$k_{32} = 3.04 \times 10^{-12} \exp(350/T) \alpha / (1 + \alpha)$ where $\alpha = 1.15 \times 10^{-31} \exp(7460/T)$
33.	DMS + NO ₃ → 2HCHO + NO ₂ + SO ₂	$k_{33} = 1.9 \times 10^{-13} \exp(500/T)$

j is given in s⁻¹; k in cm³ molecule⁻¹ s⁻¹; P is pressure in atm; T is in K; M represents N₂ or O₂ or another third molecule.

The reaction rates are from Chen and Crutzen (1994) and Lawrence et al. (1999) except reactions 29-33, which are from Atkinson et al. (1989) and Chatfield and Crutzen (1990).

$a = ; b = ka + M \times kb / (1 + M \times Kc/kb)$; $ka = 7.2e-15 \times \exp(785/T)$; $kb = 4.1e-16 \times \exp(1440/T)$; $Kc = 1.9e-33 \times \exp(725/T)$

$c = 1.3e-3 \times (T/300)^{-3.5} \exp(-11000/T) M$

Table 3: Rate Reactions for Aqueous-Phase Chemistry

R.No.	Reaction	Rate
1.	$\text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{OH}^-$	$K_w = \exp(-9.731-6710/T)$
2.	$\text{CO}_2(\text{g}) \leftrightarrow \text{CO}_2.\text{H}_2\text{O}$	$H_2 = \exp(-11.50+2420/T)$
3.	$\text{CO}_2.\text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{HCO}_3^-$	$K_3 = \exp(-18.98-1000/T)$
4.	$\text{HCO}_3^- \leftrightarrow \text{H}^+ + \text{CO}_3^{2-}$	$K_4 = \exp(-17.86-1760/T)$
5.	$\text{SO}_2(\text{g}) \leftrightarrow \text{SO}_2.\text{H}_2\text{O}$	$H_5 = \exp(-10.26+3120/T)$
6.	$\text{SO}_2.\text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{HSO}_3^-$	$K_6 = \exp(-10.97+1960/T)$
7.	$\text{HSO}_3^- \leftrightarrow \text{H}^+ + \text{SO}_3^{2-}$	$K_7 = \exp(-21.56+1500/T)$
8.	$\text{H}_2\text{SO}_4(\text{g}) \leftrightarrow \text{H}_2\text{SO}_4.\text{H}_2\text{O}$	$H_8 = \exp(-25.73+17339/T)$
9.	$\text{H}_2\text{SO}_4.\text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{HSO}_4^-$	$K_9 = 1000$
10.	$\text{HSO}_4^- \leftrightarrow \text{H}^+ + \text{SO}_4^{2-}$	$K_{10} = \exp(-13.71+2720/T)$
11.	$\text{HNO}_3(\text{g}) \leftrightarrow \text{HNO}_3.\text{H}_2\text{O}$	$H_{11} = 2.1 \times 10^5$
12.	$\text{HNO}_3.\text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{HNO}_3^-$	$K_{12} = \exp(-26.46+8700/T)$
13.	$\text{NH}_3(\text{g}) \leftrightarrow \text{NH}_3.\text{H}_2\text{O}$	$H_{13} = \exp(-7.086+3400/T)$
14.	$\text{NH}_3.\text{H}_2\text{O} \leftrightarrow \text{OH}^- + \text{NH}_4^+$	$K_{14} = \exp(-9.444-450/T)$
15.	$\text{O}_3(\text{g}) \leftrightarrow \text{O}_3.\text{H}_2\text{O}$	$H_{15} = \exp(-12.20+2300/T)$
16.	$\text{H}_2\text{O}_2(\text{g}) \leftrightarrow \text{H}_2\text{O}_2.\text{H}_2\text{O}$	$H_{16} = \exp(-10.99+6620/T)$
17.	$\text{S(IV)} + \text{O}_3 \rightarrow \text{S(VI)} + \text{O}_2$	$J_{17a} = 2.4 \times 10^4$ $J_{17b} = \exp(31.37-5530/T)$ $J_{17c} = \exp(38.84-5280/T)$
18.	$\text{S(IV)} + \text{H}_2\text{O}_2 \rightarrow \text{S(VI)} + \text{H}_2\text{O}$	$J_{18} = \exp(34.33-4751/T)$

K_w is given in M^2 ; H is in M atm^{-1} ; J_{17} is in $\text{M}^{-1}\text{s}^{-1}$; J_{18} is in $\text{M}^{-2}\text{s}^{-1}$ and T is in Kelvin. Reactions rates are from

Chen and Crutzen [1994]. The rate expression and rate constants for S(IV) with O_3 and H_2O_2 (reactions 17 and 18) are given as:

$$\begin{aligned} d[\text{S(IV)}]_{aq}/dt &= -\{J_{17a}[\text{SO}_2.\text{H}_2\text{O}] + J_{17b}[\text{HSO}_3^-] + J_{17c}[\text{SO}_3^{2-}]\} [\text{O}_3]_{aq}; \\ d[\text{S(IV)}]_{aq}/dt &= -J_{18}[\text{H}^+][\text{HSO}_3^-][\text{H}_2\text{O}_2]_{aq}/(1+k[\text{H}^+]), \text{ where } k=13 \text{ M}^{-1} \end{aligned}$$

 Table 4: Dry deposition velocities v_d (cm s^{-1})

Surface	DMS	H_2S	DMSO	MSA	SO_2	NOx	CO	O_3	H_2O_2	Sulfate Mass		Sulfate Number	
										Aitken	Accum.	Aitken	Accum.
Ocean	0.0	0.0	1.0	0.05	0.7	0.001	0.0	0.0	0.01	0.05	0.05	0.05	0.05
Land	0.0	0.0	0.0	0.20	0.20	0.01	0.04	0.0	0.01	0.20	0.20	0.20	0.20
Ice	0.0	0.0	0.0	0.20	0.20	0.0	0.0	0.0	0.01	0.20	0.20	0.20	0.20

Table 5: Wet deposition properties

Parameter	C_v	F_{aq}
DMS	0.2	Henry's law
H ₂ S	0.2	Henry's law
DMSO	0.2	Henry's law
MSA	0.5	0.7
SO ₂	0.2	Henry's law
NOx	0.0	Henry's law
CO	0.0	Henry's law
O ₃	0.2	Henry's law
H ₂ O ₂	0.2	Henry's law
Sulfate mass Aitken	0.3	0.5
Sulfate mass accum.	0.5	0.7
Sulfate number Aitken	0.2	0.3
Sulfate number accum.	0.4	0.5

F_{aq} : fraction in aqueous phase;

C_v : fraction of detrained species which
is scavenged during convective transport;

Table 6: Budget of H₂O₂ over the globe

	Processes	Global Annual
Source (mg H ₂ O ₂ m ⁻² yr ⁻¹)	HO ₂ + HO ₂	1835.8
Sinks, (mg H ₂ O ₂ m ⁻² yr ⁻¹)	H ₂ O ₂ + OH photodissociation	545.8 584.6
	Dry deposition	220.5
	Wet deposition	397.8
	Oxidation of SO ₂	87.1
Burden (mg H ₂ O ₂ m ⁻²)	Total	1835.8
Lifetime, days		5.9
		1.17

Table 7: Global Annual sulphur budgets and comparison to other models

Processes	Standard	LR91	C96	R00	LMD-ZT
Sources TgS yr ⁻¹	SO₂				
Emissions	70.8	95	96	79	64.6 18.6 3.2
DMS oxidation					
H ₂ S oxidation					
Sinks, TgS yr ⁻¹					
Dry deposition	-34.8	-32	-28	-31	-39.6 (45.8%)
Wet deposition	-1.0	-15	0.0	-20	-2.7 (3.1%)
Gas Phase	-13.1	-8	-8	-12	-12.8 (14.8%)
Aqueous Phase	-31.7	-44	-59	-56	-31.3 (36.3%)
Burden TgS yr ⁻¹	0.63	0.3	0.6	0.4	0.25
Lifetime, days	2.9	1.2	2.3	1.9	1.1
Total Sulfate					
Sources TgS yr ⁻¹					
Industrial Emissions	1.9	6	5	2	3.3
Gas Phase	13.1	8	8	12	12.8 (29%) 3.9
Aitken mode					8.9
accumulation mode					31.3 (71%)
Aqueous Phase	31.7	44	59	56	5.7
Aitken mode					25.6
accumulation mode					
Sinks, TgS yr ⁻¹					
Dry deposition	-5.7	-16	-25	-7	-6.0
Wet deposition	-41.1	-84	-75	-93	-41.4
Burden Tg S	0.72	0.8	1.1	0.6	0.63
Life Time, days	5.6	5.3	5.3	4.0	4.9
Sulfate from GPP					
Sources, TgS yr ⁻¹					
Gas Phase	-13.1				-12.8
Sinks, TgS yr ⁻¹					
Dry deposition	-0.4				-0.6
Wet deposition	-12.8				-12.2
Burden TgS yr ⁻¹	0.41				0.35
Lifetime, days	11.3				10.0
Sulfate from APP					
Sources, TgS yr ⁻¹					
Industrial Emissions	1.9				3.3
Aqueous Phase	31.7				31.3
Sinks, TgS yr ⁻¹					
Dry deposition	-5.3				-9.2
Wet deposition	-28.3				-25.4
Burden TgS yr ⁻¹	0.31				0.28
Lifetime, days	3.4				2.9

Previous studies are abbreviated as follows: LR91: Langer and Rodhe (1991); C96: Chin et al. (1996); R00: Rasch et al. (2000) and Standard: Koch et al. (2003)